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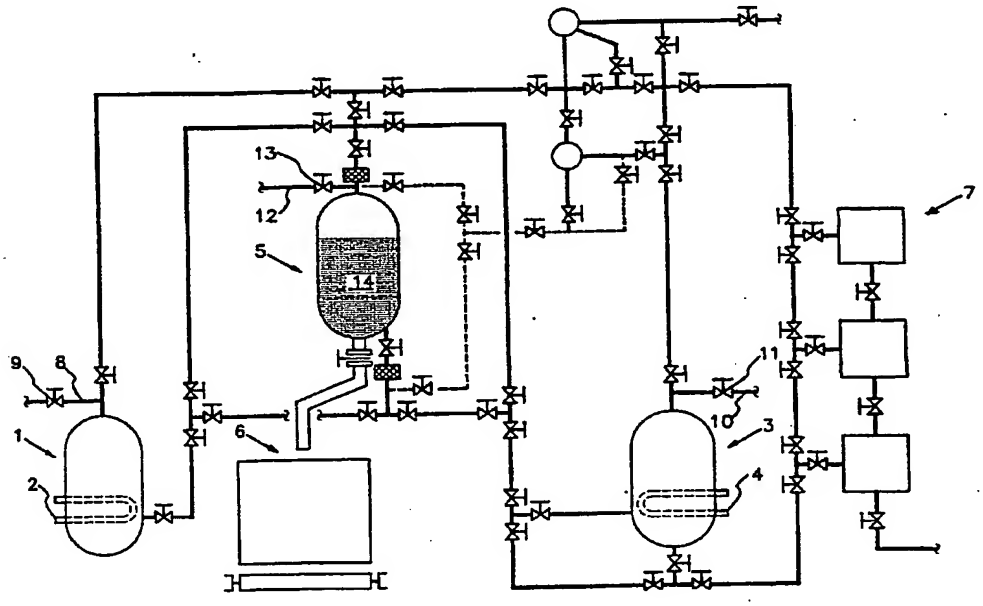

(57) Abstract

Novel foods, nutraceuticals, and pharmaceutical products are produced from conventionally known solvent extraction comprising contact of the oil-bearing material (material bed 14) with a normally gaseous solvent (vessel 1) within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid. The improvement over the conventionally known extraction process is the addition of a gas (vessel 3) into the extraction zone (vessel 5) which at a givent pressure liquifies at a higher temperature than the solvent wherein the temperature and pressure within the extraction zone is suficient to cause the solvent to liquify when the solvent is introduced into the extraction zone.

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FOOD PRODUCTS, NUTRACEUTICALS, AND PHARMACEUTICALS PRODUCED FROM SELECTIVE EXTRACTION OF CARBONACEOUS MATERIALS

Field of the Invention

The present invention relates to modified food products, nutraceuticals, and pharmaceuticals produced by a novel method for cold solvent extraction of desired compounds, such as fats, from carbonaceous products wherein the modified food products, nutraceuticals, and pharmaceuticals maintain the flavor of the original carbonaceous products treated by the cold solvent extraction process.

Background of the Invention

It is known that certain compounds found naturally in food products can have harmful effects to a persons health. The removal of these compounds, as well as the addition of other compounds which are known to have beneficial health effects, has led to much research and development to produce such modified food products. These modified food products are generally known as nutraceuticals. Examples of such nutraceuticals were set forth by ***Food Product Design*** (December 1993) in an article entitled "Nutraceutical Reality on the Horizon" by Scott Hegenhart.

For purposes of this patent the term "nutraceutical" shall mean any substance considered a food, or part of a food, with medical or health benefits, including the prevention, treatment or cure of disease.

One major problem in formulating nutraceuticals is to obtain the flavor of the food product which the nutraceutical is emulating. This problem has been more acute when oils and other fats are the compounds being removed from a food product to form

the nutraceutical. It has been believed that a significant portion of those compounds which produce the flavor of a food product are found or linked to the oils and other fats found in the food product. Thus, when using prior art methods for extraction of oils and fats from food products, the resulting food product generally did not retain the flavor of the original food product.

In copending patent application PCT/US92/11394 and in copending United States patent application 07/815,700, novel methods for selectively extracting compounds from carbonaceous materials were disclosed.

It has now been discovered that when using the cold solvent extraction methods disclosed in those applications that oils and fats can be removed, and that the nutraceutical formed has a flavor that is substantially the same as the original food product being treated.

It has also been discovered that the flavor retention can be achieved with processed foods, as well as non-processed foods when using those cold solvent extraction methods.

It has also been discovered that the oils and fats removed from a food product also retained the same or closely similar flavor characteristics which they originally had in the food product when using those cold solvent extraction methods.

Summary of the Invention

Therefore one object of this invention is to provide a nutraceutical formed by removing a substantial portion of the oil and fat content of a food product in a manner causing the nutraceutical to retain the flavor of the food product.

Another object of this invention is to provide a nutraceutical formed by removing a substantial portion of the oil and fat content of a food product using the cold solvent extraction methods of this invention.

A further object of this invention is to provide novel oils and other substances having more desirable food consumption characteristics.

A further object of this invention is to provide novel fruits, vegetables, spices, seeds, nuts, edible roots, dairy products, and processed foods from which their oil and fats have been substantially removed in a manner to retain the flavor of the original food product.

A further object of this invention is to provide novel cereal oils and de-oiled cereals.

A further object of this invention is to provide novel low fat potato and potato based food products, such as potato chips, fried potatoes.

A further object of this invention is to provide novel low fat fried and baked fish products.

A further object of this invention is to provide novel low fat fried, broiled, and roasted meat products.

A further object of this invention is to provide novel low fat cocoa products and low fat cocoa based products, such as chocolate cookies and other chocolate snacks.

A further object of this invention is to provide novel low fat dairy products and dairy based products, such as food products utilizing eggs and cheeses.

A further object of this invention is to provide novel low fat nuts, such as peanuts, almonds, and coconut.

A further object of this invention is to provide novel low fat bean products, such as jojoba beans, cocoa beans, soybean curd, and coffee beans.

A further object of this invention is to provide novel low fat spice products, such as vanilla, cinnamon, ginger, garlic, and black pepper.

A further object of this invention is to provide novel low fat fruit products, such as banana and orange peels.

A further object of this invention is to provide novel food coating product having dielectric properties promoting sticking and/or adhering to other food materials.

A still further object of this invention is to provide novel pharmaceutical products extracted from carbonaceous material by the process of this invention, such as beta carotene extracted from algae, fungi, or yeast, and proteins, such as lytic peptides and vitamins, extracted from carbonaceous material.

Other objects and advantages of this invention will become apparent from the ensuing descriptions of the invention.

Accordingly, novel foods, nutraceuticals and pharmaceutical products are provided which are produced from a solvent extraction process by contact of a normally gaseous solvent with a carbonaceous-containing material that forms a material bed within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises: introducing into the extraction zone a gas which at a given pressure liquifies at

a higher temperature than the solvent, the introduction being made under sufficient pressure to cause the temperature and pressure of the extraction zone to be sufficient to cause the solvent to liquify when the solvent is introduced to the extraction zone, then introducing the solvent to the pressurized extraction zone at a rate and at a temperature and pressure which will maintain the solvent in a liquid state in the extraction zone and in sufficient quantities to extract at least some quantity of the substance, and changing the pressure differential above and below the extraction zone during the extraction in a pulse-like fashion.

In a preferred embodiment of the present invention, the product is produced wherein the extracted compounds/solvent mixture is removed by introducing a second compound, such as nitrogen, methane, or CO_2, having dissimilar and greater vaporization conditions from the solvent which is used to not only purge the extracted compound/solvent mixture from the extraction zone, but to maintain the temperature and pressure so that the first introduced solvent is maintained in liquid form during the purging and movement to the separation zone.

In another preferred embodiment of the present invention, the product is produced by introducing into the extraction zone the gas which at a given pressure liquifies at a higher temperature than the solvent, the introduction being made after the extraction has begun and under sufficient pressure to cause the temperature and pressure of the extraction zone to remain sufficient to cause the solvent and the extracted material to

remain liquid when the solvent and the extracted material are being removed from the extraction zone.

In another preferred embodiment, the product is produced according to the process of this invention wherein air is evacuated from the extraction zone prior to contacting the solvent with the carbonaceous-containing material.

In still another preferred embodiment, the product is produced according to the process of this invention wherein a stabilizing agent is introduced to the extraction zone during the contacting of the solvent with the carbonaceous-containing material.

Brief Description of the Figures

Figures 1 through 8 each are the same simplified schematic drawing of a reaction vessel system wherein the novel products can be produced utilizing the preferred solvent extraction process.

Figure 1 indicates the principal vessels and equipment utilized in preparing the system for cold solvent extraction of the carbonaceous material placed in the extraction vessel.

Figure 2 indicates the principal vessels and equipment utilized in removing air or oxygen from the system and preparing the system for introduction of the solvent.

Figure 3 indicates the principal vessels and equipment utilized in introducing the solvent into the system.

Figure 4 indicates the principal vessels and equipment utilized in displacing the solvent and extracted oil in the reaction vessel by the inert gas.

Figure 5 indicates the principal vessels and equipment utilized in controlling the flow of propane and extracted oil mixture through the reaction vessel.

Figure 6 indicates the principal vessels and equipment utilized in pressure pulsing the reaction vessel.

Figure 7 indicates the principal vessels and equipment utilized in flushing the solvent from the reaction vessel.

Figure 8 indicates the principal vessels and equipment utilized in the removal of the solvent from the extracted oil.

Description of the Preferred Embodiments of the Invention

Any carbonaceous material can be treated to selectively remove substances by the solvent extraction method of the present invention to form novel compositions. Non-limiting examples of such carbonaceous include various beans (e.g., coffee beans, jojoba beans, cocoa beans, soybeans), cottonseed, linseed, cereals (e.g., rice bran, barley, wheat bran, and corn meal), potatoes, potato based products (e.g., potato chips, French fried potatoes), yams, cooked meat products (e.g., cooked hamburger, fried chicken), cooked fish (e.g., fried catfish), chocolate products (e.g., chocolate cookies, cocoa powder), diary products (e.g., eggs, cheeses), nuts (e.g., coconut, peanuts, almonds), spices (vanilla, black pepper), fruits (e.g, banana, orange peel, dates), vegetables (e.g., bell peppers), as well as small particle products such as food coatings (e.g., gravy flavoring made from cooked wheat and soya oil), and aquatic plants (e.g., algae, fungus, yeast). Non-limiting examples of the types of substances which can be removed from such materials include phospholipids, fats, fatty acids, alcohols, waxes, gums,

stearols, oil soluble proteins, flavonols, mineral oils, essential oils, oils from cooked or processed food, oils from earth material, PCB's, other toxins from earth materials, and pharmaceutical products (e.g., beta carotene).

Solvents suitable for use in the present invention are any solvent which is normally a liquid at extraction conditions, and in which the compound to be extracted is soluble under the reaction conditions. The selection of the appropriate solvent (or combinations of solvents) can thus be made based on its (their) known solubility characteristics. If there is to selective removal of substances, then the solubility of those substances must be considered in the selection of the solvent (or combination of solvents), as well as the operating conditions used in the process. In certain circumstances, such as when treating food products, other known characteristics of the solvent may need to be taken into account.

Without limiting the scope of this invention, the preferred embodiments are described as applied to the treatment of certain food products to remove oils and/or fats, as well as the treatment of certain plant life, both natural and genetically engineered, such as algae and fungi to produce beta carotene, omega 3, omega 6, antioxidants, peptides, vitamin or enzyme precursors, and enzymes.

Depending on the particular type substances being removed solvents suitable for use in the present invention would include any solvent which is normally a liquid at extraction conditions, or which can be converted to a liquid at extraction conditions. For the removal of oils and fats from food products to produce

a modified food product or nutraceutical, it is preferred to that the solvent be substantially odorless and tasteless. In addition preferred solvents are those which are normally gaseous at typical atmospheric conditions. That is, those which are a gas at about room temperature (about 70°F) and atmospheric pressure. Particularly preferred solvents are propane, iso-butane, and mixtures thereof; and, most preferred is propane.

The weight ratio of solvent to oil-bearing material will be from about 1:1 to 2:1, preferably from about 1.2:1 to 1.5:1. A co-solvent, such as a C_2 to C_6 alcohol or their derivatives or extensions, preferably ethanol, may be used. If a co-solvent is used it may be used in place of at least about 0.5 to 90 vol.%, preferably about 5 to 50 vol.%, and more preferably from about 5 to 25 vol.%, of the primary solvent.

Referring first to the Figure 1, a preferred vessel system is schematically illustrated which also incorporates means to remove the solvent from the recovered oils extracted from the carbonaceous material. More particularly, there are three principal vessels: a solvent (preferably, propane) storage vessel 1 equipped with conventional heating or cooling coils 2 to maintain the desired temperature of the solvent within vessel 1, an inert dissimilar gas storage vessel 3 also equipped with conventional heating or cooling coils 4 to maintain the desired temperature of the dissimilar gas in vessel 3, and a reaction vessel 5. As is explained below the heating or cooling coils 2 and 4 are also used to aid in the pressure pulsing which is utilized in the reaction vessel 5. There is also a treated product storage vessel 6, and if desired, an extracted

oil/solvent mixture purification unit 7 for separating the solvent from the extracted oil. In an alternate embodiment vessels 3 and 5 could be combined into a single vessel having two zones separated from one another by an appropriate filter which would maintain the treated carbonaceous material in one zone.

By "inert gas" is meant a gas which will not cause a deleterious reaction of the extracted oil or extracted material. The preferred inert gas is nitrogen, carbon dioxide or methane. More preferred is nitrogen. The gas replaces the solvent/oil mixture in the extraction zone and maintains substantially the same pressure throughout the solvent/oil removal step. This prevents freezing of the extracted material. It is preferred that the inert gas which is introduced into the extraction zone to displace the solvent/oil mixture be heated. That is, that it be at a temperature from about -20°F to 140°F, preferably at a temperature from about 100°F to 120°F. This heated inert gas can enhance the recovery of any residual oil and solvent left in the extracted material.

It is also preferred that in designing the reactor vessel and in selecting the solvents to be used, the specific gravities of the substances to be removed and the specific gravity of the solvents be as different as possible. This has found to be beneficial in the separation of the oil and solvent from each other, as well as the oil bearing material, during the pulsing stages. For example the large differential in the weight of propane and oil causes the propane to separate from the oil and move upward in a purified form to contact more oil still bound in the rice bran while the extracted oil rapidly moves toward the

separation zone for removal. This reduces the amount of solvent needed to remove the oil and/or reduces the amount of separation of solvent from the extracted oil.

Referring to Figure 1 a preferred method of producing the food, nutraceutical and pharmaceutical products is disclosed. Vessel 1 is filled with about 10% nitrogen and about 90% propane via line 8 and through valve 9 from an exterior source not shown. Valve 9 is then closed. Vessel 3 is filled with nitrogen via line 10 and through valve 11 from an exterior source not shown. Valve 11 is then closed. The carbonaceous material to be processed is then introduced via line 12 and through valve 13 into vessel 5 where it settles toward the bottom of vessel 5 to form a material bed 14.

Turning now to Figure 2, the air or oxygen in vessel 5 is evacuated by opening valves 15, 16, 17, 18, and 19. In order to minimize explosion, if propane is selected as the solvent, and to reduce oxidation of the carbonaceous material. Vacuum pump 20 is then activated to pull a vacuum in vessel 5. The evacuated air and oxygen is pulled through lines 21, 22 and is vented to the atmosphere through line 23. Valves 15, 16, 17, 18, and 19 are then closed and vacuum pump 20 is shut down. Nitrogen from vessel 3 is then introduced into vessel 5 in an amount to raise the pressure within vessel 5 to about 100 psi. This is accomplished by opening valves 24, 25, 26, 27, 28, 29, 30, and 31. Once sufficient nitrogen has been introduced, these valves are then closed. It is preferred that the nitrogen be at elevated temperatures, for example at a temperature from about 80° to 400°F, but which does not heat the material beyond 140°F,

preferably from about 55° to 120°F, during the heat transfer. These can be controlled by coils 2. This hot nitrogen flush can also assist in evacuating the extraction zone of air as well as heating, or drying, the oil-bearing material.

While the hot nitrogen gas can be used to dry the material, it may also be dried by any other appropriate means, such as by heating it by conventional means, including the use of microwaves. Furthermore, after flushing the extraction zone with nitrogen, the nitrogen can be used to pressurize the extraction zone so that when the normally gaseous solvent propane is introduced into the extraction zone it is immediately transformed to the liquid state to prevent refrigeration freezing.

Referring now to Figure 3, the nitrogen in vessel 5 is displaced with the propane solvent. This is achieved by opening valves 31, 32, 33, 34, and 35. Propane can now flow from the bottom of vessel 1 via lines 36, 37, and 38 through filter 58 and into the bottom of the material bed in vessel 5. The propane will pass through material bed 14 extracting oil as it goes through material bed 14. The extracted oil and propane mixture will then exit vessel 5 through filter 60. Filter 60 is sized to prevent the material bed material from exiting vessel 5. With valves 15, 40, 41, 42, 43, 44 opened, the propane and extracted oil will flow to vessel 3 via lines 21, 45, 46 and 47.

Referring now to Figure 4, compressor 39 is activated to compress nitrogen in vessel 3. As nitrogen is removed from vessel 3 the propane and extracted oil from line 47 displace the nitrogen in vessel 3. The nitrogen flows through compressor 39 and routed to vessel 1 by opening values 24, 25, 26, 48, 18, 17,

49, and 50. This permits the nitrogen to then flow through lines 51, 52, 53, 22, and 54 to vessel 1.

It is also within the scope of this invention that the normally gaseous propane be introduced into vessel 5 already in a liquid state. The nitrogen can also be used to pressurize the extraction zone so that as the normally gaseous propane enters the extraction zone, it is converted to its liquid form. Typically, the extraction temperature will be from about ambient temperature, up to, but not including, the temperature at which degradation, or denaturing, of the proteins of the oil-bearing material is initiated. It is also desirable to protect the vitamins against degradation. This temperature will typically range from about ambient temperature to about 140°F, preferably from about 60°F to 130°F, more preferably from about 70°F to 120°F, most preferably from about 70°F to about 110°F. For heat sensitive material such as dried egg yolks it is preferred that the temperature be 60°-90°F. It is within the scope of this invention to operate the extraction zone at a temperature and/or pressure which will selectively remove the oils, but leave any substances such as gums and waxes in the extracted oil-bearing material, or to selectively extract the phospholipid gums and waxes with the heavier oil fractions. Such a temperature will typically be less than about 80°F at about atmospheric pressure. Of course, the temperature may vary somewhat at different pressures. In addition, these temperatures may vary for any given oil-bearing material and solvent combination, and the precise conditions are within the skill of those in the art given the teaching herein. After the oil has been removed, it is then

possible to similarly treat the remaining material, but at slightly elevated temperatures and/or pressures conditions to remove the waxes and gums. The above stated conditions are the preferred conditions when the oil-bearing material is rice bran and the solvent is propane. Since the de-oiled rice bran is a commercially important product it is preferred that the temperature not be so high that the proteins and vitamins of the rice bran are destroyed during the extraction process. The pressure maintained in the extraction zone will be a pressure which is effective for maintaining the solvent as a liquid, and to drive the oil/solvent mixture rapidly through the vessel. While this pressure will be dependent on such things as the particular solvent and temperature employed, for propane it will typically range from less than atmospheric pressures to about 250 psi, preferably from about -30" Hg to 200 psi, more preferably from about 100 psi to 140 psi.

Referring now to Figure 5, the propane flow from vessel 1 is now directed toward the top of vessel 5 via lines 36, 55, and 21 and through filter 60. To accomplish this valves 32, 33, 56, 57 and 15 are opened, and valves 16 and 40 are closed. The propane flows through material bed 14 and extracts additional oil. This mixture of propane and extracted oil then pass through filter 58 which is also sized to prevent passage of the material bed particles. The mixture is then allowed to flow through lines 75, 45, and 46 to vessel 3 by opening valve 73, 74, 42, 43, and 44.

Compressor 39 is used to add nitrogen from vessel 3 to vessel 1, and to maintain the pressure in vessel 1 above the

pressure in vessel 3 to create the desired flow of propane and extracted oil mixture through vessel 5. The nitrogen will flow through valves 24 and 25 in line 51, and then through valve 26 in line 52 to compressor 39. From compressor 39 it flows through valve 48, 18, 17, 49, and 50 in lines 53, 22 and 54 to vessel 1.

Vessel 5 can also be subjected to conditions which will repeatedly stress and relax the oil-bearing material and/or solvent molecules. This is believed to create a washing effect that enhances the ability of the solvent to extract the oil from the material. In addition it is believed that such pressure pulsing aids in the separation of the heavier oil from the lighter solvent after the oil has been extracted from the material and while it is flowing toward the bottom of the reactor. This pulsing is effected to create pressure differentials between the top and bottom of the extraction zone of at least 0.25 psi. It is believed that the pulsing pressure alternately increases and decreases the solvent density, and thus changes the solvents ability to support heavier oil molecules and aiding the extracted oils to flow and separate. The pressure differential can be as great as will permit, under the temperature and pressure conditions of the material bed, the solvent passing through the exit port of the reactor to remain as a liquid.

This pressure differential can also be created by heating and cooling of vessel 5 or by actuating and de-actuating a piston or diaphragm in the pressure or solvent line. This can create pressure differences through the entire system by the selection of valves to open or close. The stressing and relaxation

conditions can also be caused by sonification; i.e., by subjecting the ingredients of the extraction zone to sonic energy.

In a particularly preferred method a second solvent or inert gas is introduced to the top surface of the extraction zone to increase the pressure and then briefly open a valve in the separation zone to cause the second solvent or inert gas to displace part of the propane/oil mixture through the bottom filter. In this manner it acts as a dynamic fluid piston which enlarges to completely occupy vessel 5 and displace the solvent/extracted oil mixture. This action allows the bed to be comprised of much smaller particles than has generally heretofore be used in solvent extraction processes. There is no need to pre-pelletize such particles before treatment.

This also allows the utilization of the forces of polarity in combination to extract different materials at the same time by using pressure from the second gas. By selecting a second solvent having a different polarity, or co-solvents of varying polarity strengths, that solvent, or co-solvents, can be used to remove different substances, such as cholesterol from egg powders.

Referring now to Figure 6, the pressure pulsing of vessel 5 can be achieved by allowing nitrogen to flow from vessel 3 through valves 27, 28, 29, 30 and 31 in by-pass lines 61 and 62 and filter 58 and its material bed 14. Alternatively, the nitrogen can be introduced at the top of vessel 5 by allowing the nitrogen to flow from vessel 3 through valves 27, 28, 77, 76 in by-pass lines 61 and 62 and into the top of material bed 14. If

one wishes to add nitrogen at the top of material bed 14 it is preferred that the nitrogen also flow thorough filter 60.

The pulsing of nitrogen through filter 58 and into the bottom of the material bed also helps to prevent channeling and filter blockage. Multiple pulsing can be done if desired.

The pulsing can be done before the solvent and extracted oil is removed from vessel 5, or after some of the solvent and extracted oil is removed. In any event, once the pulsing is completed and after opening and closing the appropriate values, the solvent and additional extracted oil in vessel 5 is directed toward vessel 3 by flowing nitrogen from vessel 1 via lines 54, 22, 53 to compressor 39 and then via lines 52, 61, and 78 into the top of vessel 5. The pressure of vessel 5 is maintained at about 100 psi.

Referring now to Figure 7, after the solvent has been removed from vessel 5 by displacement with nitrogen, the nitrogen in vessel 5 is pulled through filter 60 and directed through compressor 39 via lines 21, 22 and 53, and then back into vessel 5 through filter 58 via lines 52, 61, 62 and 38. Next circulate nitrogen from vessel 1 through compressor 39 via lines 54, 22 and 53 while pulling a vacuum by vacuum pump 20 through vessel 5. After all propane has been flushed from vessel 5, sufficient nitrogen is left in vessel 5 to bring vessel 5 to atmospheric pressure. The rest of the nitrogen is sent to a storage tank or to vessel 63 utilizing vacuum pump 20 to direct the nitrogen through lines 64 and 65 and valves 66, 67, 68 and 69. The various open valves are closed before opening vessel 5.

In an alternate embodiment propane which may be entrapped in the treated solids may be removed by circulating heated nitrogen at reduced pressures in vessel 5 sufficient to vaporize the propane from the liquid to gaseous state and then removing the propane/nitrogen mixture to purification unit 7 by vacuum pump 20 and compressor 39.

Vessel 5 is then emptied of the treated carbonaceous material by opening valve 70 and allowing the material to discharge into bin 71 where can be conveyed to storage by a conventional conveyor system 72.

Referring now to Figure 8, the extracted oil in vessel 3 is transported to the oil purification unit 7 and propane mixture where any propane or nitrogen can be separated from the extracted oil by conventional separation techniques. The purified extracted oil can then be recovered via line 73. If desired the recovered extracted oil can be transported to a separation unit to be fractionated if desired.

In a preferred embodiment the propane and extracted oil mixture from vessel 3 flows through valves 80, 81, 82, and 83 in lines 94, 95, and 96 and into separating vessel 91. The heavier oil will settle to the bottom of vessel 91 at which time valve 98 can be opened and the extracted oil can flow through line 73.

If the extracted oil can not be damaged by some heat, vessel 91 could be heated to allow the now gaseous propane to flow through valve 89 and into propane storage vessel 92.

If it is desired to mix the propane in vessel 92 with the nitrogen in vessel 63 for transporting to another vessel,

appropriate valves 86, 87, 88, 89 and/or 69 can be opened or closed depending on the flow direction desired.

It is also within the scope of this invention that solvent vapor be passed through the de-oiled material either in place of the inert gas or following the passage of inert gas. This solvent vapor will act to remove at least a portion of the residual oil/ solvent mixture left in the de-oiled material.

In those situations where the oil-bearing material is one which is unstable because of the production of fatty acids, such as rice bran, a stabilizing agent can be added to vessel 5 via line 12. Any appropriate means can be used to add the stabilizing agent. That is, it can be sprayed directly onto the oil-bearing material prior to the material being introduced into the extraction zone. It can also be introduced into the extraction zone either directly, (as shown in the figure) or in combination with the solvent. Rice bran, the preferred oil-bearing material, upon milling, activates lipolytic enzymes which catalyze the production of free fatty acids. These free fatty acids cause the bran to become rancid. Non-limiting examples of stabilizers which can be used to stabilize rice bran include an inert gas such as nitrogen, food grade acids and alcohols, preferably ethanol, mercaptans, and enzyme inhibitors, protein, and/or peptides. Preferred are food grade acids and alcohols, non-limiting examples of which include citric acid, ascorbic acid, lactic acid, gluconic acid, malic acid, ethanol and the like. More preferred are citric acid and ascorbic acid, with ascorbic acid being most preferred.

Various food and plant products were treated in accordance with this invention to reduce the oil and fat content to less than 1% by weight so as to produce novel food, nutraceuticals and pharmaceutical products. The novel food and nutraceuticals produced were subjected to flavor tests to determine if there was any change in their flavor from the original untreated material. Universally, it was unexpectedly found that the novel food and nutraceutical products had a flavor that was the same or substantially the same as the original untreated material.

Each of the tested food, nutraceutical and pharmaceutical products were produced utilizing propane and nitrogen in the extraction procedure set forth above. The temperatures and pressures in the extraction vessel 5 were maintained at 40°-60°F and 0-150 psi. The food and nutraceutical products produced which were then taste tested include cooked and/or processed foods (Frito Lay® Cheese Paitos®, Frito Lay® potato chips, Zapp's® potato chips, McDonald's® french fries, Mars® Snickers® chocolate candy bar, Mars® peanuts from M&M's®, roasted peanuts, chicken fried with seasoned flour batter, turkey fried in vegetable oil, roasted turkey, catfish fried in seasoned flour batter, seasoned baked catfish, grilled McDonald's® hamburger patty, Country Flavors® gravy powder), dairy foods (Kraft® parmesan cheese, Mid-American® parmesan cheese, Kraft® cheddar cheese, eggs, tofu), nuts (raw coconut flakes, Bakers® sweetened coconut, almonds, raw ground peanuts), beans (Nestle® cocoa baking powder, Hershey® cocoa baking powder, roasted coffee beans, jojoba beans), spices (vanilla, ground cinnamon, ground black pepper, ginger powder, cut up garlic), fruits (orange peel,

bananas, kumquats), grains (raw rice bran, soya flake) and plants (Red Horse® chewing tobacco). The tobacco was treated to remove the tars and nicotine compounds. Pharmaceuticals which were tested included lecithin from egg yolk, tocopherol and tocotrienol from rice bran oil, gamma-oryzanol from rice bran oil, omega-3 and omega-6 from fish oil, taxol from pine needles, and beta carotene derived from green and orange algae and sweet potatoes.

From three to forty taste testers were used for each product. Each taste tester was asked to compare the novel food and nutraceutical products to the original material, and to rate the flavor as the same, close or noticeably different. The results of these taste tests were:

Product Description	Number of Testers By Flavor Same	Slight	Noticed	Total
Kraft®/Mid American® parmesan cheese	27	13	0	40
Kraft® cheddar cheese	22	18	0	40
Bakers® sweetened chocolate	6	6	0	12
Zapp's® potato chips	8	2	0	10
Frito Lay® cheese Paitos®	6	4	0	10
Frito Lay® potato chip	8	2	0	10
Nestle® cocoa baking powder	3	3	0	6
Hershey® cocoa baking powder	4	3	0	7
Mars® Snickers® candy bar	3	2	0	5
M&M peanuts from Snickers®	2	2	0	4
Roasted peanut meal	2	3	0	5
Ground cinnamon	4	1	0	5
Ground restaurant grade black pepper	2	1	0	3
Ginger powder	2	1	0	3
Cut-up garlic	5	2	0	7

Roasted coffee beans	3	2	0	5
Automatic brew coffee beans	4	1	0	5
Orange peels	2	1	0	3
Bananas	1	2	0	3
Chicken fried with seasoned flour batter	5	2	0	7
Turkey fried with vegetable oil	1	2	0	3
Baked Fish	0	3	0	3
Fish fried with seasoned flour batter	2	1	0	3
Broiled McDonald® hamburger patty	3	5	0	8
Raw rice bran	3	8	0	11
Soya flake	1	2	0	3
Green algae beta carotene	5	0	0	5
Orange algae beta carotene	5	0	0	5
Red Horse® chewing tobacco	3	2	0	5

It is not understood why flavor retention is so great when oil is extracted by the process described herein. It is now believed that oils and fats may be necessary to develop flavor, but are not necessary to retain the developed flavors. It is also believed that the formed compounds primarily responsible for flavors are to some extent masked by the oil and fats in the food products. This is supported by the fact that for some of the products tested above the slight change in flavor was the creation of a stronger awareness of flavor awareness, rather than a weaker awareness of flavor. Because of the gentle manner (low temperatures and pressures) in which the oil and fats are removed, it is believed that these flavor compounds are not destroyed by the extraction process. It is also believed that propane does not chemically react at the temperatures and

pressures used with the flavor compounds to the extent that other solvents may react. This would explain why there is not consistent flavor results when hexane, alcohols and similar solvents are utilized.

It has also unexpected been found that the extracted oils retain the flavor of the original product from which they were extracted.

What Is Claimed Is:

1. A food product, nutraceutical or pharmaceutical obtained by a process for extracting oils from oils-containing material by contact of a normally gaseous substantially odorless and tasteless solvent with the oils that forms a material bed within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises:

(a) introducing into the extraction zone a gas which at a given pressure liquifies at a higher temperature than the solvent, the introduction being made under sufficient pressure to cause the temperature and pressure of the extraction zone to be sufficient to cause the solvent to liquify when the solvent is introduced to the extraction zone, and

(b) then introducing the solvent to the pressurized extraction zone at a rate and at a temperature and pressure which will maintain the solvent in a liquid state in the extraction zone and in sufficient quantities to extract at least some quantity of the oils.

2. A food product, nutraceutical or pharmaceutical obtained by a process for extracting oils from oils-containing material by contact of a normally gaseous solvent with the oils that form a material bed within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises changing the pressure differential above and below the extraction zone during the extraction in a pulse-like fashion.

3. A food product, nutraceutical or pharmaceutical obtained by a process for extracting a oils from oils-containing material by contact of a normally gaseous solvent with the oils that forms a material bed within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises introducing into the extraction zone a gas which at a given pressure liquifies at a higher temperature than the solvent, the introduction being made after the extraction has begun and under sufficient pressure to cause the temperature and pressure of the extraction zone to remain sufficient to cause the solvent and the oils to remain liquid when the solvent and the oils are being removed from the extraction zone.

4. A food product, nutraceutical or pharmaceutical obtained by a process for extracting a oils from oils-containing material by the use of a solvent which comprises:

(a) introducing the oils-containing material into an extraction zone;

(b) introducing into the extraction zone a gas which at a given pressure liquifies at a higher temperature than the solvent, the introduction being made under a pressure and at a temperature to cause the temperature and pressure of the extraction zone to be sufficient to cause the solvent to liquify when the solvent is introduced to the extraction zone;

(c) introducing the solvent into the extraction zone and into contact with the material to extract the oils from the material;

(d) introducing into the upper portion of the extraction zone a second gas which at a given pressure liquifies at a higher

temperature than the solvent, at a higher pressure than the pressure in the extraction zone in a manner to create a pressure differential between the top and the bottom of the extraction zone and to maintain the solvent in liquid form in the extraction zone;

(e) removing a portion of the extracted material and solvent from the extraction zone in a manner to maintain the solvent in liquid form in the extraction zone;

(f) repeating steps (d) and (e) until all the solvent has been removed from the extraction zone; and

(g) separating the solvent from the extracted oils.

5. A food product, nutraceutical or pharmaceutical obtained by a process for extracting a oils from oils-containing material by contact of a normally gaseous solvent with the oils that forms a material bed within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises evacuating air from the extraction zone prior to contacting the solvent with the oils.

6. A food product, nutraceutical or pharmaceutical obtained by a process for extracting a oils from a carbonaceous-containing material by contact of a normally gaseous solvent with the oils that forms a material bed within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises introducing a stabilizing agent to the extraction zone during the contacting of the solvent with the carbonaceous-containing material.

7. A food product, nutraceutical or pharmaceutical obtained by a process for extracting a oils from carbonaceous-containing material by contact of a normally gaseous solvent with the carbonaceous-containing material that forms a material bed within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises:

(a) introducing into the extraction zone a gas which at a given pressure liquifies at a higher temperature than the solvent, the introduction being made under sufficient pressure to cause the temperature and pressure of the extraction zone to be sufficient to cause the solvent to liquify when the solvent is introduced to the extraction zone,

(b) then introducing the solvent to the pressurized extraction zone at a rate and at a temperature and pressure which will maintain the solvent in a liquid state in the extraction zone and in sufficient quantities to extract at least some quantity of the oils, and

(c) changing the pressure differential above and below the extraction zone during the extraction in a pulse-like fashion.

8. A food product, nutraceutical or pharmaceutical obtained by a process for extracting a oils from carbonaceous-containing material by contact of a normally gaseous solvent with the carbonaceous-containing material that forms a material bed within an extraction zone maintained at temperatures and

pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises:

(a) introducing into the extraction zone a gas which at a given pressure liquifies at a higher temperature than the solvent, the introduction being made under sufficient pressure to cause the temperature and pressure of the extraction zone to be sufficient to cause the solvent to liquify when the solvent is introduced to the extraction zone,

(b) then introducing the solvent to the pressurized extraction zone at a rate and at a temperature and pressure which will maintain the solvent in a liquid state in the extraction zone and in sufficient quantities to extract at least some quantity of the oils, and

(c) introducing into the extraction zone a gas which at a given pressure liquifies at a higher temperature than the solvent, the introduction being made after the extraction has begun and under sufficient pressure to cause the temperature and pressure of the extraction zone to remain sufficient to cause the solvent and the oils to remain liquid when the solvent and the oils are being removed from the extraction zone.

9. A food product, nutraceutical or pharmaceutical obtained by a process for extracting a oils from carbonaceous-containing material by contact of a normally gaseous solvent with the carbonaceous-containing material that forms a material bed within an extraction zone maintained at temperatures and

pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises:

(a) evacuating air from the extraction zone prior to contacting the solvent with the carbonaceous-containing material,

(b) introducing into the extraction zone a gas which at a given pressure liquifies at a higher temperature than the solvent, the introduction being made under sufficient pressure to cause the temperature and pressure of the extraction zone to be sufficient to cause the solvent to liquify when the solvent is introduced to the extraction zone, and

(c) then introducing the solvent to the pressurized extraction zone at a rate and at a temperature and pressure which will maintain the solvent in a liquid state in the extraction zone and in sufficient quantities to extract at least some quantity of the oils.

10. A food product, nutraceutical or pharmaceutical obtained by a process for extracting a oils from carbonaceous-containing material by contact of a normally gaseous solvent with the carbonaceous-containing material that forms a material bed within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises:

(a) introducing into the extraction zone a gas which at a given pressure liquifies at a higher temperature than the solvent, the introduction being made under sufficient pressure to cause the temperature and pressure of the

extraction zone to be sufficient to cause the solvent to liquify when the solvent is introduced to the extraction zone,

(b) then introducing the solvent to the pressurized extraction zone at a rate and at a temperature and pressure which will maintain the solvent in a liquid state in the extraction zone and in sufficient quantities to extract at least some quantity of the oils, and

(c) introducing a stabilizing agent to the extraction zone during the contacting of the solvent with the carbonaceous-containing material.

11. A food product, nutraceutical or pharmaceutical obtained by a process for extracting a oils from carbonaceous-containing material by contact of a normally gaseous solvent with the carbonaceous-containing material that forms a material bed within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises

(a) introducing into the extraction zone a gas which at a given pressure liquifies at a higher temperature than the solvent, the introduction being made after the extraction has begun and under sufficient pressure to cause the temperature and pressure of the extraction zone to remain sufficient to cause the solvent and the oils to remain liquid when the solvent and the oils are being removed from the extraction zone, and

(b) changing the pressure differential above and below the extraction zone during the extraction in a pulse-like fashion.

12. A food product, nutraceutical or pharmaceutical obtained by a process for extracting a oils from carbonaceous-containing material by contact of a normally gaseous solvent with the carbonaceous-containing material that forms a material bed within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises

(a) evacuating air from the extraction zone prior to contacting the solvent with the oils, and

(b) changing the pressure differential above and below the extraction zone during the extraction in a pulse-like fashion.

13. A food product, nutraceutical or pharmaceutical obtained by a process for extracting a oils from carbonaceous-containing material by contact of a normally gaseous solvent with the carbonaceous-containing material that forms a material bed within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises:

(a) evacuating air from the extraction zone prior to contacting the solvent with the carbonaceous-containing material, and

(b) introducing into the extraction zone a gas which at a given pressure liquifies at a higher temperature than the solvent, the introduction being made after the extraction has begun and under sufficient pressure to cause the temperature and pressure of the extraction zone to remain sufficient to cause the solvent and the oils to remain liquid when the solvent and the oils are being removed from the extraction zone.

14. A food product, nutraceutical or pharmaceutical obtained by a process for extracting a oils from carbonaceous-containing material by contact of a normally gaseous solvent with the carbonaceous-containing material that forms a material bed within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises

(a) changing the pressure differential above and below the extraction zone during the extraction in a pulse-like fashion, and

(b) introducing a stabilizing agent to the extraction zone during the contacting of the solvent with the carbonaceous-containing material.

15. A food product, nutraceutical or pharmaceutical obtained by a process for extracting a oils from carbonaceous-containing material by contact of a normally gaseous solvent with the carbonaceous-containing material that forms a material bed within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises:

(a) introducing into the extraction zone a gas which at a given pressure liquifies at a higher temperature than the solvent, the introduction being made after the extraction has begun and under sufficient pressure to cause the temperature and pressure of the extraction zone to remain sufficient to cause the solvent and the oils to remain liquid when the solvent and the oils are being removed from the extraction zone, and

(b) introducing a stabilizing agent to the extraction zone during the contacting of the solvent with the carbonaceous-containing material.

16. A food product, nutraceutical or pharmaceutical obtained by a process for extracting a oils from carbonaceous-containing material by contact of a normally gaseous solvent with the oils that forms a material bed within an extraction zone maintained at temperatures and pressures that cause the solvent to remain a liquid during the extraction, the improvement to which comprises:

(a) evacuating air from the extraction zone prior to contacting the solvent with the carbonaceous-containing material, and

(b) introducing a stabilizing agent to the extraction zone during the contacting of the solvent with the carbonaceous-containing material.

17. A food product, nutraceutical or pharmaceutical according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, or 16 wherein the carbonaceous material is selected from a group consisting of: Frito Lay® Cheese Paitos®, Frito Lay® potato chips, Zapp's® potato chips, McDonald's® french fries, Mars® Snickers® chocolate candy bar, Mars® peanuts from Snickers®, roasted peanuts, chicken fried with seasoned flour batter, turkey fried in vegetable oil, roasted turkey, catfish fried in seasoned flour batter, seasoned baked catfish, grilled McDonald's® hamburger patty, Country Flavors® gravy powder, Kraft® parmesan cheese, Mid-American® parmesan cheese, Kraft® cheddar cheese, eggs, tofu, raw coconut flakes, Bakers® sweetened

coconut, almonds, raw ground peanuts), Nestle® cocoa baking powder, Hershey® cocoa baking powder, roasted coffee beans, jojoba beans, spices vanilla, ground cinnamon, ground black pepper, ginger powder, cut up garlic, orange peel, bananas, kumquats, raw rice bran, soya flake, Red Horse® chewing tobacco lecithin from egg yolk, tocopherol and tocotrienol from rice bran oil, gamma-oryzanol from rice bran oil, omega-3 and omega-6 from fish oil, taxol from pine needles, and beta carotene derived from green and orange algae and sweet potatoes.

18. A food product, nutraceutical or pharmaceutical according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, or 16 wherein the solvent is propane and the gas is nitrogen.

19. A food product, nutraceutical or pharmaceutical according to claim 17 wherein the solvent in propane and the gas is nitrogen.

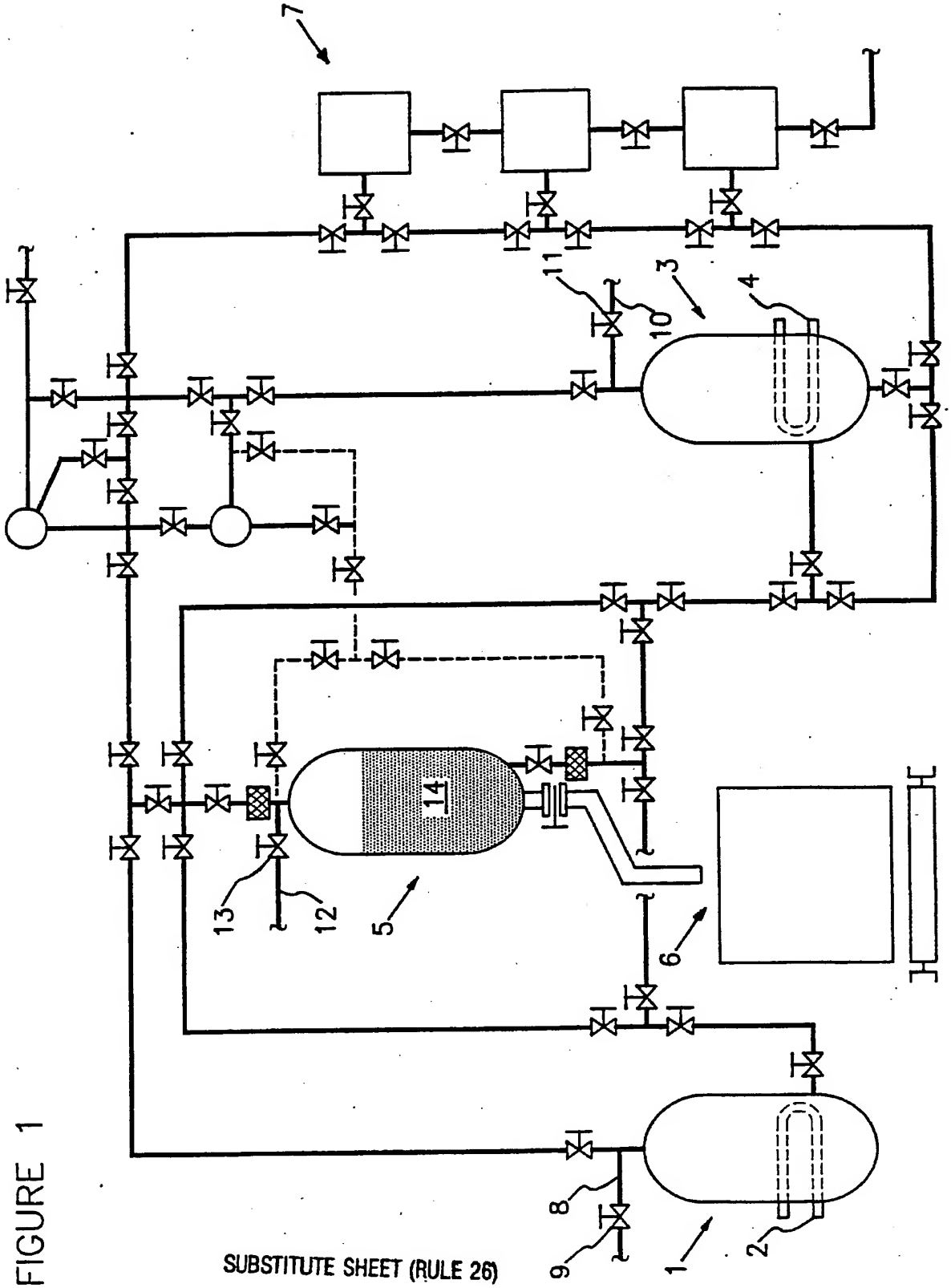

FIGURE 1

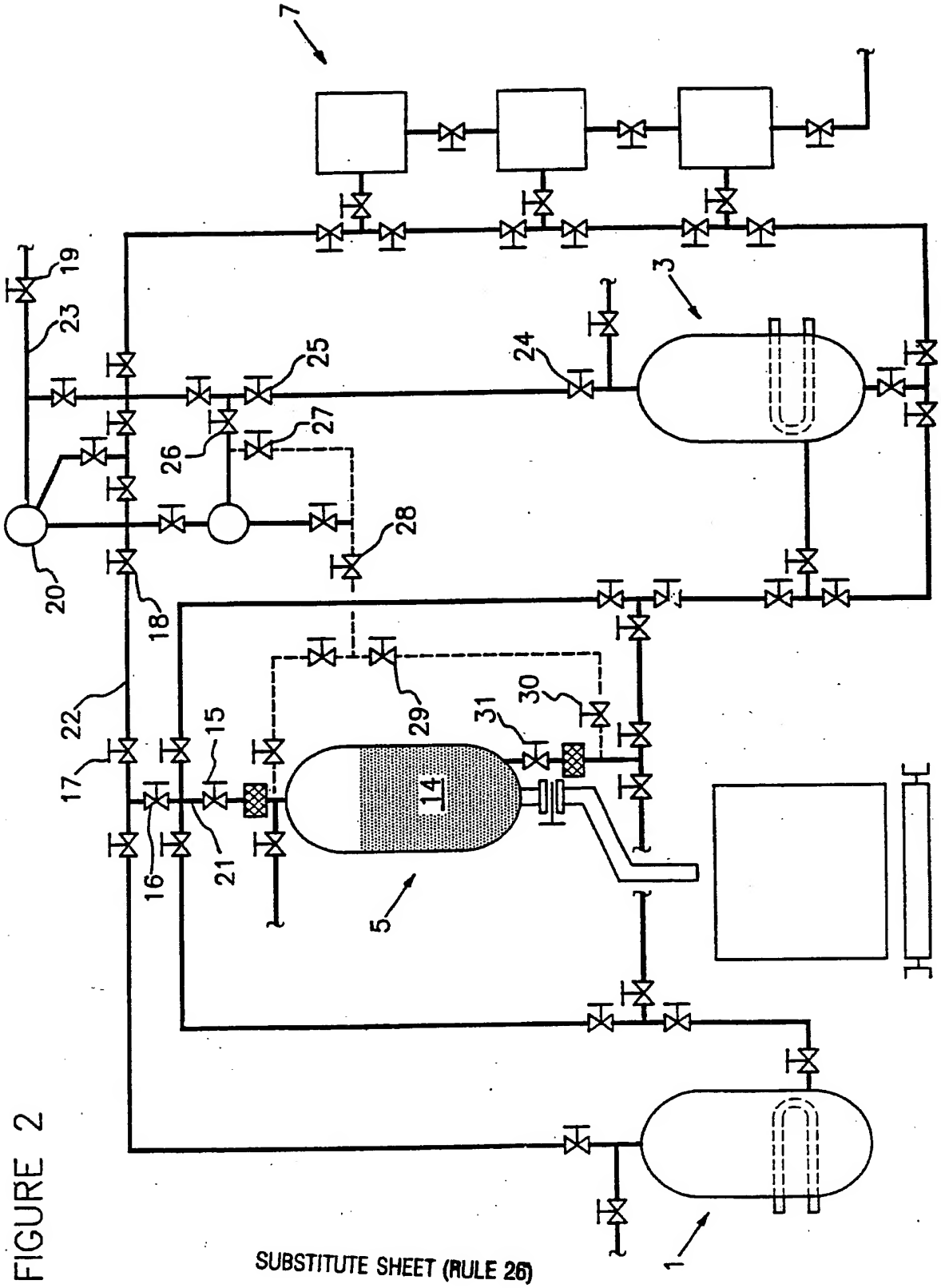

FIGURE 2

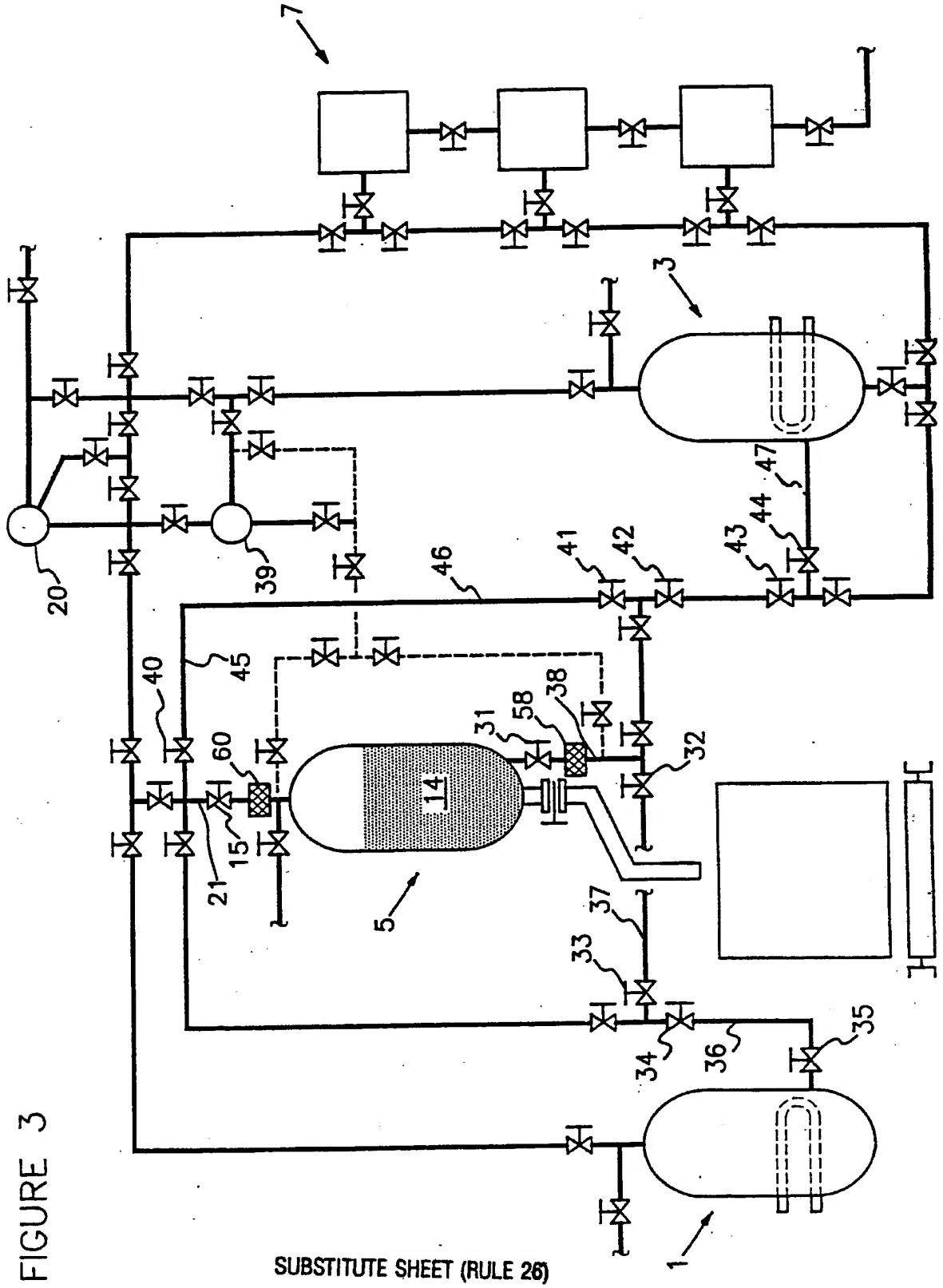
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FIGURE 3

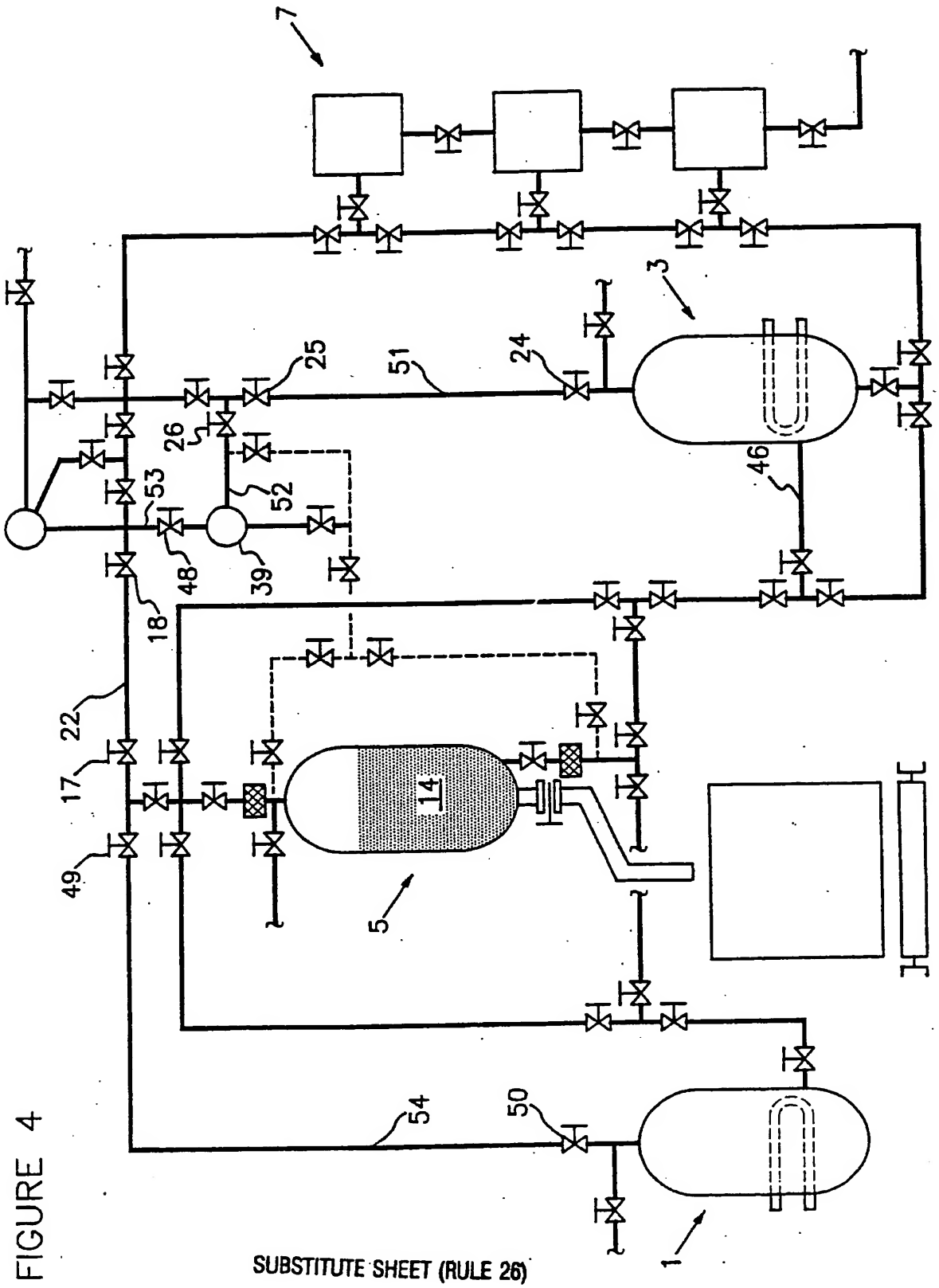

FIGURE 4

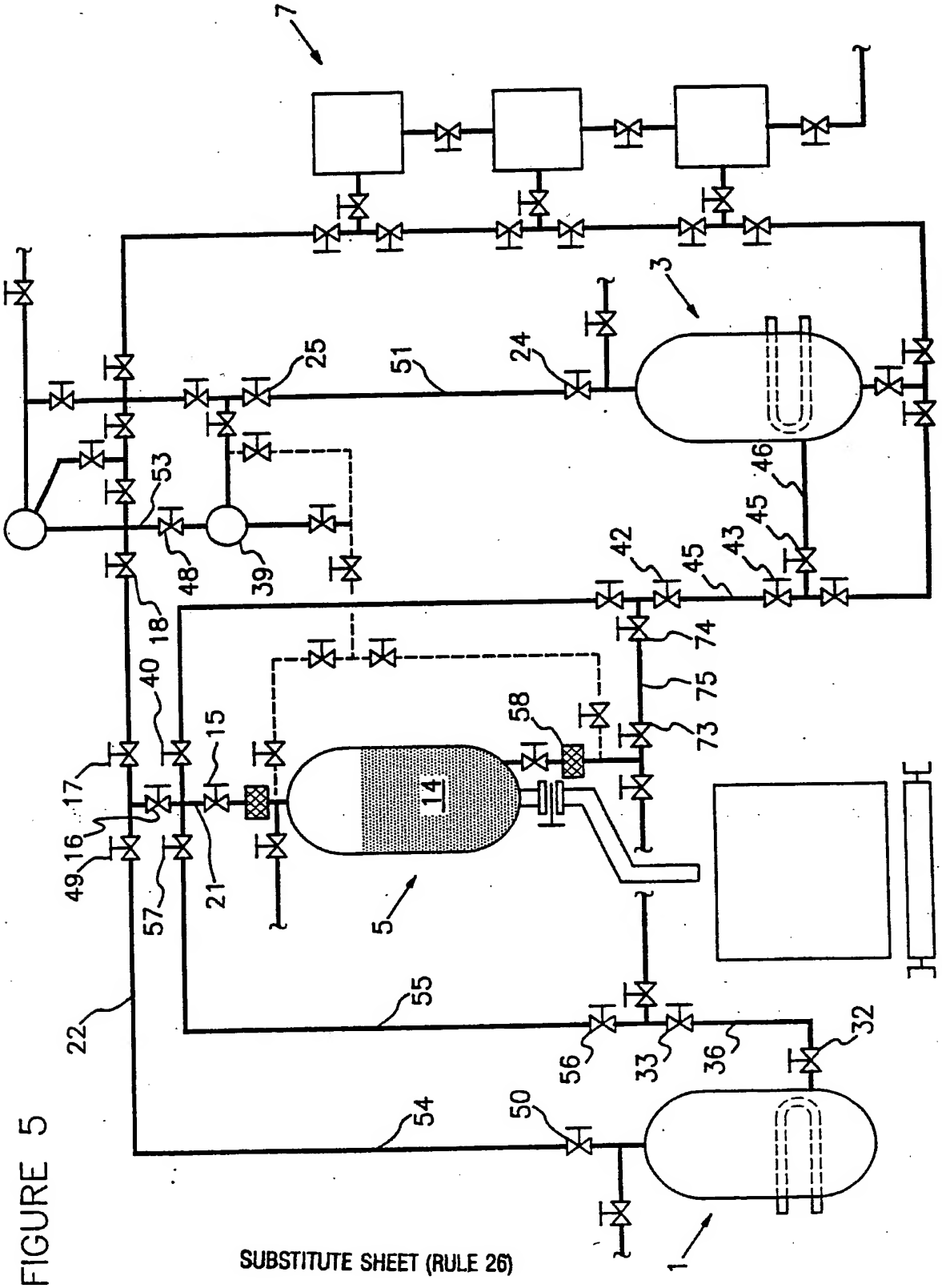
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FIGURE 5

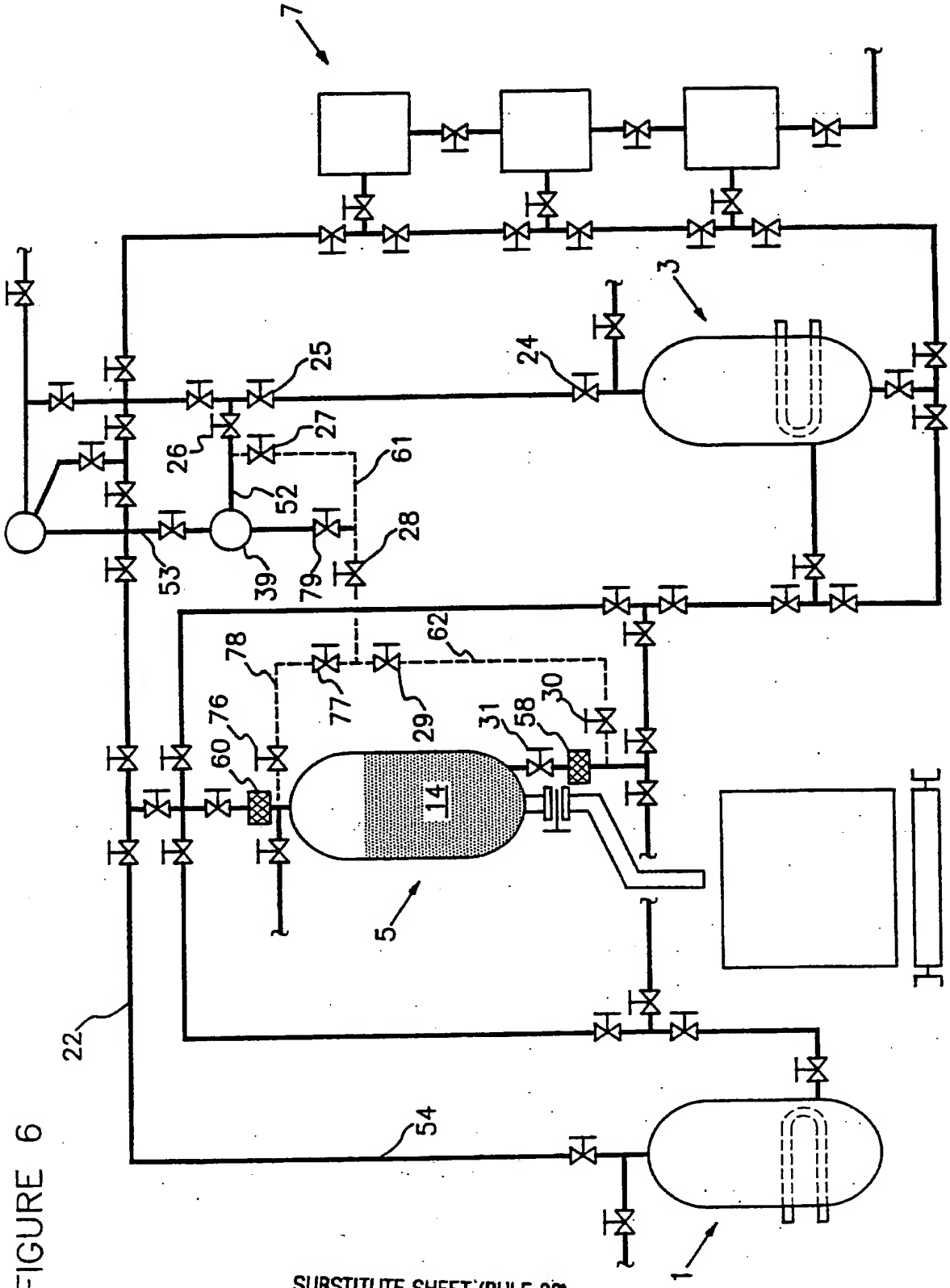

FIGURE 6

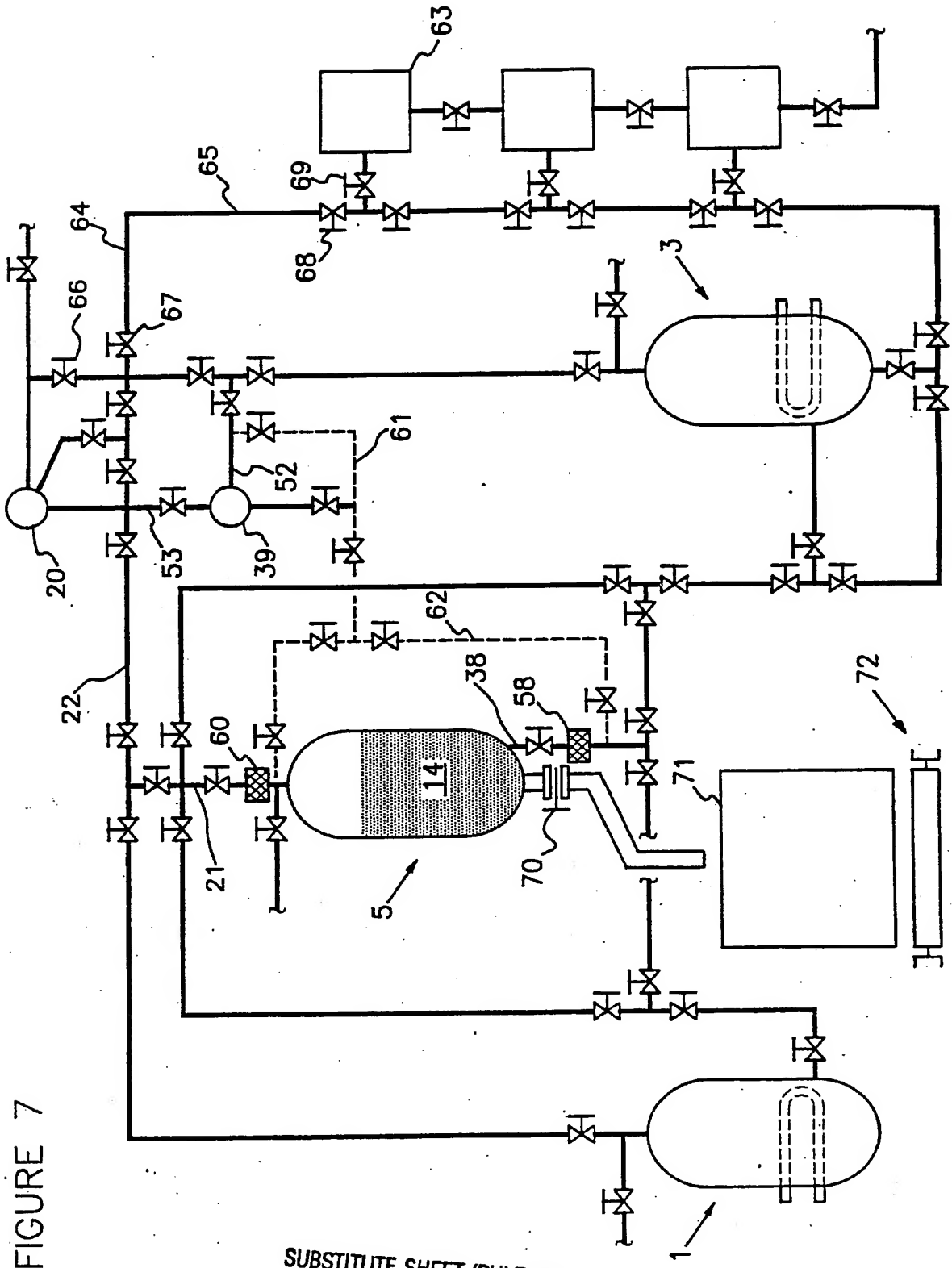

FIGURE 7

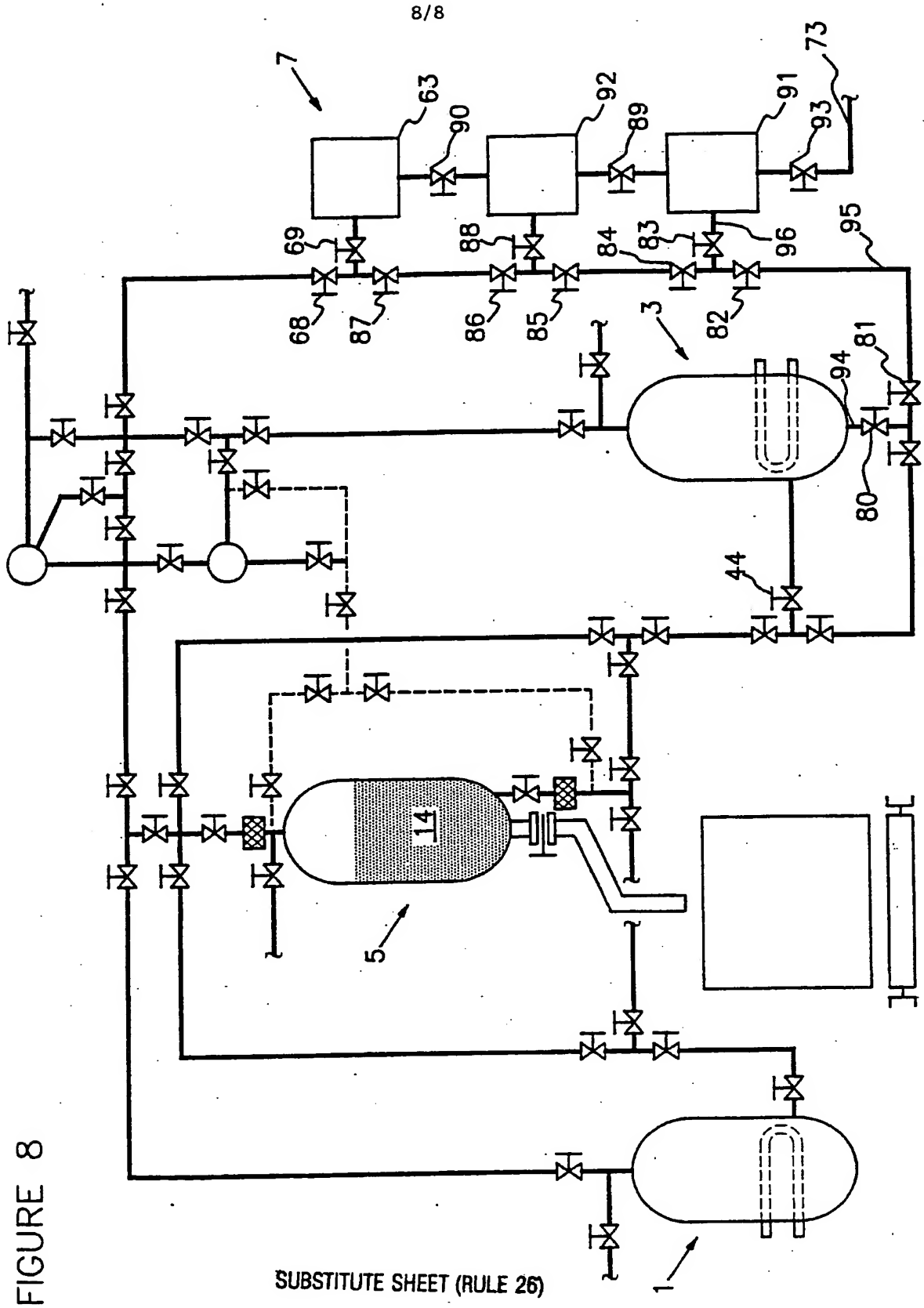
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FIGURE 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/00231

A. CLASSIFICATION OF SUBJECT MATTER
IPC(5) :A23L 1/00; C07C 1/00;
US CL :425/425,429,474; 554/9,11,12,16,20,21,22,185,205,209
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S. : 425/425,429,474
554/9,11,12,16,20,21,22,185,205,209

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
APS, CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
&, E	US, A, 5,281,732 (Franke) 25 January 1994, entire document.	1-19
X	US, A, 4.331,695 (Zosel) 25 May 1982, entire document.	1-12
Y		1-12
X	US, A, 5,,041,245 (Benado) 20 August 1991, entire document.	1-12
Y		1-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be part of particular relevance
"E" earlier document published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
25 MAY 1994

Date of mailing of the international search report
13 JUN 1994

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